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मानक

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IS 8587 (1993): Acid grade fluorspar for chemical industry
[CHD 1: Inorganic Chemicals]



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“Knowledge is such a treasure which cannot be stolen”

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भारतीय मानक

रासायनिक उद्योगों के लिए अम्ल ग्रेड फ्लुओरस्फार — विशिष्ट
(पहला पुनरीक्षण)

Indian Standard

ACID GRADE FLUORSPAR FOR
CHEMICAL INDUSTRY — SPECIFICATION

(First Revision)

UDC 622.363.412 : 66

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BUREAU OF INDIAN STANDARDS
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FOREWORD

This Indian Standard (First Revision) was adopted by the Bureau of Indian Standards, after the draft finalized by the General Inorganic Chemicals Sectional Committee had been approved by the Chemical Division Council.

Fluorspar (fluorite), chemically known as calcium fluoride (CaF_2), is used in chemical industry after beneficiation initially for the production of hydrofluoric acid either in anhydrous state or in the form of solution which is used in the manufacture of various fluorine compounds including fluorocarbons and safety refrigerants on the one hand and cryolite (sodium aluminium fluoride), aluminium fluoride and other fluorine based chemicals on the other. High purity hydrofluoric acid is the starting point in the synthesis of these chemicals. The purity of hydrofluoric acid depends upon the grade of fluorspar used in its manufacture.

The term 'acid grade fluorspar' has come to be recognized as that beneficiated fluorspar which is suitable for manufacture of pure hydrofluoric acid, and which is low in silica, calcium carbonate, sulphur and other impurities contents because of their deleterious effects on the technical, economic and corrosive aspects of hydrofluoric acid manufacture.

Acid grade fluorspar is normally a finely ground flotation product obtained by beneficiating mineral fluorspar which has calcium fluoride (CaF_2) as the main constituent alongwith silica, pyrites, barytes (BaSO_4), etc as impurities.

This standard was originally published in 1977 and is being revised to change the title to acid grade fluorspar for chemical industry from the ordinary fluorspar as this is the correct nomenclature used universally to distinguish the acid grade fluorspar suitable for making anhydrous hydrofluoric acid from other grades of fluorspar. In this revision, two grades of acid grade fluorspar have been prescribed based on their application in the manufacture of various fluorine based chemicals. The requirement for calcium fluoride has been raised to 97.5 percent by mass, *Min* for Grade 1 material, suitable for the manufacture of aluminium fluoride. The requirements for other characteristics such as calcium, barium, sulphur, phosphorus, mixed oxides, chloride, beryllium and organic matters have also been revised as better quality of the material is now available in the country and the world over. The packing and marking clauses have also been modified.

An alternate complexometric method for the determination of calcium fluoride and a new photometric method for the estimation of silica have also been incorporated as referee methods. New comprehensive and simple methods for the determination of sulphur and organic matter have been prescribed deleting the existing methods.

The composition of the committee responsible for the formulation of this standard is given at Annex C.

For the purpose of deciding whether a particular requirement of this standard is complied with, the final value, observed or calculated, expressing the result of a test or analysis, shall be rounded off in accordance with IS 2 : 1960 'Rules for rounding off numerical values (revised)'. The number of significant places retained in the rounded off value should be the same as that of the specified value in this standard.

Indian Standard

ACID GRADE FLUORSPAR FOR CHEMICAL INDUSTRY—SPECIFICATION

(First Revision)

1 SCOPE

This standard prescribes requirements and methods of sampling and test for acid grade fluorspar suitable for chemical industry.

NOTE — Fluorspar for use in metallurgical industry is covered under a separate Indian Standard, IS 4574 : 1989.

2 REFERENCES

The Indian Standards listed below are necessary adjuncts to this standard:

IS No.	Title
265 : 1993	Hydrochloric acid (<i>fourth revision</i>)
1070 : 1992	Reagent grade water (<i>third revision</i>)
2246 : 1963	Methods of sampling for fluorspar (fluorite)
2411 : 1963	Methods of chemical analysis of fluorspar (fluorite)
4574 : 1989	Fluorspar for use in metallurgical industries (<i>second revision</i>)

3 GRADES

The material shall be of following two grades:

Grade 1 — suitable for manufacture of aluminium fluoride, and

Grade 2 — suitable for manufacture of fluorocarbons, cryolite and other fluorides.

4 REQUIREMENTS

4.1 Description

The material shall be either in the form of a filter cake or dry powder.

4.2 Size Analysis

When tested according to the method prescribed in Annex A, the material shall have size

analysis as agreed to between the purchaser and the supplier.

NOTE — The size analysis of fluorspar for chemical industry is generally as follows:

	Percent by Mass
a) Retained on 500-micron IS Sieve	Nil
b) Retained on 212-micron IS Sieve	10, Max
c) Retained on 75-micron IS Sieve	25, Max

4.3 The material shall comply with the requirements prescribed in Table 1 when tested according to the methods prescribed in IS 2411: 1963 and Annex B of this standard. Reference to the relevant clauses of IS 2411 : 1963 and Annex B is given in col 5 and 6 of Table 1.

5 PACKING AND MARKING

5.1 Packing

In bulk, acid grade fluorspar is usually transported loose in a wet cake form in ships, wagons, or trucks. When it is transported in a dry powdery form, it shall be packed in gunny or polyethylene bags to prevent transit loss.

5.2 Marking

The gunny/polyethylene bags shall be conspicuously marked with the following details:

- a) Name and description of the material;
- b) Net mass of the material;
- c) Indication of the source of manufacture: and
- d) Lot number.

6 SAMPLING

Representative samples of the material shall be drawn as prescribed in IS 2246 : 1963.

Table 1 Requirements for Acid Grade Fluorspar for Chemical Industry
(Clause 4.3)

Sl No.	Characteristic	Requirement		Method of Test, Ref to CI No. in	
		Grade 1	Grade 2	Annex B	IS 2411 : 1963
(1)	(2)	(3)	(4)	(5)	(6)
i)	Free moisture, percent by mass, <i>Max</i>	10.0	10.0	B-2	—
ii)	Calcium fluoride (as CaF_2), percent by mass, <i>Min</i>	97.5	96.0	B-3	5
iii)	Calcium (as CaCO_3), percent by mass, <i>Max</i>	0.7	1.0	—	6
iv)	Barium (as BaSO_4), percent by mass, <i>Max</i>	0.20	0.5	—	10
v)	Phosphorus (as P_2O_5), percent by mass, <i>Max</i>	0.02	0.23	B-4	—
vi)	Sulphur (as S), percent by mass, <i>Max</i>	Nil	0.03	B-5	—
vii)	Mixed oxides (as R_2O_3), percent by mass, <i>Max</i>	0.6	1.5	—	9
viii)	Organic matter, percent by mass, <i>Max</i>	0.03	0.25	B-6	—
ix)	Silica (as SiO_2), percent by mass, <i>Max</i>	0.7	1.0	B-7	8
x)	Chlorides	—	To pass test	B-8	—
xi)	Beryllium	To pass test	To pass test	B-9	—

NOTE — The requirements from Sl No. (ii) to (xi) are on dry basis.

ANNEX A

(Clause 4.2)

SIZE ANALYSIS OF ACID GRADE FLUORSPAR FOR CHEMICAL INDUSTRY

A-1 PROCEDURE

A-1.1 Distribute the weighed quantity of the material, dried as in B-2.1, on the coarsest sieves of a nest consisting of 500-micron, 212-micron and 75-micron IS Sieves of about 20 cm diameter each. Crumble any lump of dried material by means of a rubber tipped rod. Fix the nest of sieves tightly in a mechanical shaker, following the appropriate instructions supplied by the

manufacturer of the machine. Shake for exactly 25 minutes and then remove the sieves from the shaker.

A-1.2 Weigh the amount of the material remaining on each sieve and the fines passing into the receiver. Any granules which lodge in the meshes of a sieve shall be rubbed through on to the next finer sieve and shall be weighed with the material retained in the finer sieve.

ANNEX B

(Clause 4.3 and Table 1)

METHODS OF TEST FOR ACID GRADE FLUORSPAR FOR CHEMICAL INDUSTRY

B-1 QUALITY OF REAGENTS

B-1.1 Unless specified otherwise, pure chemicals and distilled water (see IS 1070 : 1992) shall be employed in tests.

NOTE — 'Pure chemicals' shall mean chemicals that do not contain impurities which affect the results of analysis.

B-2 DETERMINATION OF MOISTURE

B-2.1 Procedure

Weigh accurately about 100 g of the material and transfer to a petri dish. Uncover the dish and put it in an oven maintained at $105 \pm 2^\circ \text{C}$ for 2 hours. Transfer the dish to a desiccator.

Replace the cover, allow to cool and weigh. Repeat the process till constant mass is obtained. Use the dried material for all subsequent tests.

B-2.2 Calculation

Moisture, percent by mass = $\frac{M_2 - M_3}{M_2 - M_1} \times 100$

where

M_2 = mass in g of the material and the weighing bottle before drying,

M_3 = mass in g of the material and weighing bottle after drying, and

M_1 = mass in g of the weighing bottle.

B-3 DETERMINATION OF TOTAL CALCIUM IN CALCIUM FLUORIDE (CaF_2)

B-3.0 Two methods are prescribed namely, volumetric method and complexometric method. In case of dispute, the complexometric method shall be the referee method.

B-3.1 Volumetric Method

B-3.1.1 The method is the same as prescribed in 5 of IS 2411 : 1963.

B-3.2 Complexometric Method

B-3.2.0 Outline of the Method

The sample is decomposed by digesting with nitric acid and perchloric acid and the fluorine is expelled by fuming. The residue is dissolved in dilute hydrochloric acid, the solution made alkaline and the calcium titrated with standard EDTA solution. Calcium present as carbonate is determined in a separate sample with EDTA solution, after extracting the former with dilute acetic acid. A correction for calcium fluoride, solubilized by dilute acetic acid digestion, is applied by determining the fluoride in the acetic acid extract by fluoride ion selective electrode. The calcium fluoride content is then calculated.

B-3.2.1 Apparatus

B-3.2.1.1 *Air oven* — capable of maintaining a temperature of $100 \pm 10^\circ\text{C}$.

B-3.2.1.2 *Polyethylene beakers* — 100 ml capacity.

B-3.2.2 Reagents

B-3.2.2.1 *Dilute acetic acid solution* — 10 percent (v/v). Mix 1 volume of glacial acetic with 10 volumes of water.

B-3.2.2.2 *Calcium carbonate* — high purity (containing 99.95 percent by mass, *Min* of CaCO_3).

B-3.2.2.3 *Standard ethylene diamine tetraacetic acid, disodium salt (EDTA) solution* — 0.025 N. Dissolve 9.306 g of EDTA in water, transfer

to a 1 000-ml volumetric flask, dilute to the mark and mix.

B-3.2.2.4 *Dilute hydrochloric acid* — 2 percent.

B-3.2.2.5 *Dilute hydrochloric acid* — 1 percent.

B-3.2.2.6 *Hydroxynaphthol blue indicator*

Grind 0.2 g of the salt with 50 g of sodium chloride.

B-3.2.2.7 *Potassium acetate buffer solution*

Dilute 283 ml of glacial acetic acid to 1 200 ml with water. While cooling and stirring, add 50 percent potassium hydroxide solution to adjust the pH to 5.0 (approximately 350 ml of potassium hydroxide solution is required).

B-3.2.2.8 *Potassium hydroxide solution* — 22.5 percent (m/v).

Dissolve 225 g of potassium hydroxide in water and dilute to 1 000 ml. Store the solution in a plastic bottle.

B-3.2.2.9 *Potassium hydroxide solution* — 50 percent (m/v).

Dissolve 500 g of potassium hydroxide (KOH) in water and dilute to 1 000 ml. Store the solution in a plastic bottle.

B-3.2.2.10 *Standard sodium fluoride solution*

Dissolve 0.221 0 g of sodium fluoride in water in a polyethylene beaker and dilute to 1 000 ml in a volumetric flask. Store the solution in a stoppered polyethylene bottle. One millilitre of this solution contains 0.10 mg of fluorine (as F) and is stable for about six months time.

B-3.2.2.11 *Triethanolamine solution*

Mix 50 ml of triethanolamine ($\text{NC}_6\text{H}_{15}\text{O}_3$) with 50 ml of water.

B-3.2.3 Standardization

B-3.2.3.1 Weigh 2.497 0 g of calcium carbonate (dried at 110°C for 1 h and cooled in a desiccator) and transfer to a 600-ml beaker. While covered, cautiously add 75 ml of dilute hydrochloric acid (**B-3.2.2.6**) to the beaker and warm. Cool, transfer to a 1 000-ml volumetric flask, dilute to the mark with water, and mix. One millilitre of this solution contains 1.0 mg of calcium (as Ca). Transfer a 50.00 ml aliquot of this solution to a 400-ml beaker, add 5 ml of triethanolamine solution (**B-3.2.2.11**), dilute to 200 ml, make just alkaline with 22.5 percent (m/v) potassium hydroxide solution, using a strip of litmus paper, and then add an additional 15 ml of 22.5 percent (m/v) potassium hydroxide solution. Add 0.2 g of hydroxynaphthol blue indicator (**B-3.2.2.6**) and titrate immediately with 0.025 M EDTA solution. At the equivalence point, the colour changes from pink to blue. Determine the

calcium equivalent of the EDTA solution as follows:

$$1 \text{ ml of EDTA solution} = \frac{50}{V} C \text{ mg of calcium}$$

where

V = millilitres of EDTA solution used.

NOTE 1 — If a sample with a known calcium fluoride content (as CaF_2) is available, the standardization with calcium carbonate can be omitted. The standard calcium fluoride sample should then be carried through all steps of the procedure.

B-3.2.3.2 Sample preparation

Pulverize the material to facilitate it to pass through 75-micron IS Sieve.

B-3.2.4 Procedure

B-3.2.4.1 Determination of total calcium

Transfer approximately 0.50 g of the material to a small weighing bottle, previously dried at about $105 \pm 2^\circ\text{C}$. Dry the bottle and its contents for 1 h at 105°C to 110°C . Stopper the bottle and cool to room temperature in a desiccator. Momentarily release the cap to equalize the pressure and weigh the stoppered bottle to nearest 0.1 mg. Repeat the drying and weighing till a constant mass is obtained. Transfer the sample to a 400-ml beaker and to weigh the capped bottle to the nearest 0.1 mg. The difference between the two masses is the mass of sample taken for analysis.

a) Decomposition of sample

Add 5 ml of nitric acid to the beaker, cover with a watch glass, and digest on a hot plate. Cool the watch glass, add 5 ml of perchloric acid and evaporate first to fumes of perchloric acid. When decomposition appears to be complete, tilt the cover and evaporate carefully to complete dryness. Allow to cool, add 5 ml of hydrochloric acid, dilute to approximately 50 ml with water and heat until all the soluble salts have dissolved. This is the main solution.

NOTE 2 — If an insoluble residue remains, filter through a fine textured paper, and wash the paper thoroughly with hot hydrochloric acid (B-3.2.2.4), ignite the paper and residue in a platinum crucible, and treat the insoluble residue again with nitric acid and perchloric acid as in sample decomposition. Combine this solution with the main filtrate. If the volume exceeds 90 ml, evaporate it to about 80 ml and cool.

b) Transfer the solution to a 100-ml volumetric flask, dilute to the mark and mix. Transfer an appropriate aliquot (20.00 ml in the range from 80 to 100 percent by mass of calcium fluoride and 25.00 ml in the range from 40 to 80 percent of calcium fluoride) to a 400-ml beaker. Add 5 ml of triethanolamine solution. Make the solution just alkaline with 22.5 percent (m/v)

potassium hydroxide solution and add an additional 15 ml of 22.5 percent (m/v) potassium hydroxide solution. Titrate with EDTA solution as described in B-3.2.3.

c) Multiply this titre value by C (B-3.2.3.1) to obtain milligrams of calcium in the aliquot.

d) Calculation

$$\text{Total calcium, percent by mass, } T = \frac{10 \times M}{a \times b}$$

where

T = total calcium present,

m = milligrams of calcium in the aliquot,

a = millilitres of aliquot taken for the test, and

b = mass in g of the material taken for the test.

B-3.2.4.2 Determination of soluble calcium

a) Calibration

Transfer 10 ml of acetic acid into a series of seven 100-ml polyethylene beakers and add 20 ml of potassium acetate buffer (see Note 3). Then add standard sodium fluoride solution and water in quantities indicated below:

Test	Standard Fluoride Solution (ml)	Fluoride Content (mg)	Water (ml)
1	0	0	5
2	0.5	0.05	4.5
3	1.0	0.10	4.0
4	2.0	0.20	3.0
5	3.0	0.30	2.0
6	4.0	0.40	1.0
7	5.0	0.50	0

Stir the solution, immerse the electrodes and wait for 3 to 5 minutes for potential to reach equilibrium. Record the potential in millivolts. Plot millivolts (linear scale) versus fluoride concentration in milligrams (log scale) on a semilog paper.

NOTE 3 — Potential measurements in calibration standards and sample should be carried out concurrently.

b) Weigh 1.00 g of the material and transfer to a 250-ml beaker. Add 20 ml of acetic acid and digest at just below boiling point for 60 minutes. Cool, filter through a fine-textured filter paper and wash five times with acetic acid, collecting the filtrate and washings into a 50-ml volumetric flask. Dilute the contents to mark with water.

c) Pipette out a 25-ml aliquot into a 400-ml beaker and evaporate to dryness. Redissolve the residue in 1 to 2 ml of hydrochloric acid and dilute to 200 ml with water. Add 5 ml of

triethanolamine and proceed as in total calcium determination [see 3.2.4.1 (b)]. Record the titre value. Calculate milligrams of calcium (X) in the 50-ml volume by multiplying the titre value (in millilitres) by $2C$ (see B.3.2.3.1).

Transfer a 10 ml aliquot into a 100-ml polyethylene beaker, add 20 ml of potassium acetate buffer solution and 5 ml of water (see Note 3), and mix (pH should be 5.0). Measure the potential in millivolts using reference and the fluoride ion-selective electrodes. Multiply milligrams of fluoride found in the aliquot by 5.273 7 to get calcium equivalent in milligrams (Y) of calcium fluoride in 50-ml volume. The difference ($X - Y$) in milligrams represents soluble calcium in acetic acid.

Soluble calcium, percent by mass,

$$S = (X - Y) \times 0.1$$

B.3.2.5 Calculation

Calcium fluoride, percent

$$\text{by mass (as CaF}_2\text{)} = (T - S) \times 1.948$$

where

T = total calcium percent by mass found in B.3.2.4.1 (a), and

S = soluble calcium percent found in B.3.2.4.2 (b).

B-4 DETERMINATION OF PHOSPHORUS (AS P_2O_5)

B-4.0 Outline of the Method

Sample is fused with sodium carbonate-boric acid mixture and the fused mass is evaporated to dryness with perchloric acid to remove fluorine. The residue is dissolved in water and diluted to a known volume. To an aliquot of this solution, ammonium molybdate solution is added to form phosphomolybdic acid complex which is reduced to molybdenum blue and the intensity of blue colour is measured photometrically.

B-4.1 Apparatus

B-4.1.1 Platinum Dish — 100-ml capacity.

B-4.1.2 Photoelectric Colorimeter — with cells of 2-cm path length and a filter of 795 nm length.

B-4.2 Reagents

B-4.2.1 Sodium Carbonate — Anhydrous.

B-4.2.2 Boric Acid

B-4.2.3 Perchloric Acid — 60 percent (v/v).

B-4.2.4 Ammonium Molybdate Solution — 0.26 g/l.

Dissolve 10 g of ammonium molybdate [$(NH_4)_6 Mo_7 O_{24} \cdot 4H_2O$] in 100 ml of water.

Add slowly 220 ml of dilute sulphuric acid [$1:1 (v/v)$] and 70 ml of water. Allow to cool and mix thoroughly.

B-4.2.5 Reducing Solution

B-4.2.5.1 Dissolve 0.25 g of 1-amino, 2-naphthol 4 sulphonic acid and 0.5 g anhydrous sodium sulphite (Na_2SO_3) in about 70 ml of water.

B-4.2.5.2 Dissolve 24 g of anhydrous sodium bi-sulphite ($Na_2S_2O_5$) in about 100 ml of water.

Mix solutions described in B-4.2.5.1 and B-4.2.5.2 and dilute to 200 ml with water. Filter, if necessary and store in a cool and dark place.

B-4.2.6 Ascorbic Acid Solution — 2.5 percent in water (freshly prepared).

B-4.2.7 Standard Phosphate Solution I — corresponding to 100 mg of phosphorus (as P_2O_5) per litre.

Weigh accurately 1.917 5 g of pulverized dry potassium dihydrogen phosphate, dissolve in little water and transfer quantitatively into a 1 000-ml measuring flask. Dilute to the mark and mix. Transfer 25 ml of this solution to a 250-ml measuring flask, dilute to the mark and mix. One millilitre of this solution contains 0.1 mg of phosphorus (as P_2O_5).

B-4.2.8 Standard Phosphate Solution II — corresponding to 5 mg of phosphorus (as P_2O_5) per litre.

Transfer 25 ml of standard phosphate solution I (see B-4.2.7) into a 500-ml measuring flask, dilute to the mark, and mix. One millilitre of this solution corresponds to 0.005 mg (5 micrograms) of phosphorus (as P_2O_5).

B-4.3 Procedure

B-4.3.1 Weigh 1 g of finely powdered sample in a platinum dish, add 3 g of sodium carbonate, 3 g of boric acid and mix the contents thoroughly. Fuse the mass at $800^\circ C$ for 40 minutes. Allow to cool.

B-4.3.2 Add 25 ml of perchloric acid to the dish and evaporate the mass nearly to dryness on a sand bath. Allow to cool.

B-4.3.3 Add about 50 ml of water and heat to dissolve the salt. Allow to cool and transfer the solution into a 100-ml measuring flask. Dilute to the mark and mix.

B-4.3.4 Transfer 25-ml aliquot into a 100-ml measuring flask, add 10 ml of ammonium molybdate solution and 5 ml of reducing solution, while stirring the contents after each addition. Dilute to mark and mix.

B-4.3.5 Place the flask in boiling water for 15 minutes and cool it with running water.

B-4.3.6 Transfer the solution into the cell of the colorimeter and carry out photometric measurement after having adjusted the instrument to zero absorbance against water.

B-4.3.7 Blank Test

Carry out a blank test by the same procedure using the same quantities of all reagents but without the sample.

B-4.3.8 Preparation of Calibration Graph

Into a series of 100-ml measuring flasks, transfer 1, 2, 4, 6, 8 and 20 ml of phosphate standard solution II (B-4.2.8). Add 2 ml of perchloric acid and about 50 ml of water and mix. Then proceed exactly as mentioned in (B-4.3.4), (B-4.3.5), and (B-4.3.6) and measure the absorbance values of the standard solutions. Plot a graph having the quantities in mg of phosphorus (as P_2O_5) in the standard solution as abscissae and the corresponding absorbance values as the ordinates.

B-4.4 Calculation

Determine the quantities of phosphorus (as P_2O_5) corresponding to the absorbance reading of the test sample solution and blank test solution from the calibration graph.

B-4.4.1 Phosphorus

$$\text{percent by mass} = \frac{(M_1 - M_2) \times 0.4}{M}$$

where

M_1 = mass in mg of phosphorus (as P_2O_5) in the test sample solution,

M_2 = mass in mg of phosphorus (as P_2O_5) in the blank test solution, and

M = mass in mg of the material taken for the test.

B-5 DETERMINATION OF SULPHUR (AS S)

B-5.0 Outline of the Method

Sulphur is first converted to hydrogen sulphide, by treatment with hydrochloric acid in the presence of stannous chloride and then treated with cadmium acetate solution to precipitate cadmium sulphide. This is acidified with hydrochloric acid to release hydrogen sulphide which is determined by iodometric titration.

B-5.1 Apparatus

B-5.1.1 Krupp Apparatus for Sulphur Determination — See Fig. 1.

B-5.1.2 Gas Washing Bottle — 250-ml capacity.

B-5.2 Reagents

B-5.2.1 Absorption Solution

Dissolve 50 g of cadmium acetate and 100 g of sodium acetate in 500 ml of glacial acetic acid and make up the solution to 2 000 ml with water.

B-5.2.2 Potassium Iodate-Iodide Solution — 0.1 N.

Dissolve 3.567 g of potassium iodate in a little quantity of water, add about 40 g of potassium iodide and dilute to 1 000 ml.

B-5.2.3 Sodium Thiosulphate Solution — 0.1 N.

B-5.2.4 Stannous Chloride Solution — 10 percent (m/v).

Dissolve 10 g of stannous chloride in 100 ml of hot concentrated hydrochloric acid.

B-5.2.5 Concentrated Hydrochloric Acid — See IS 265 : 1993.

B-5.2.6 Hydrochloric Acid Solution — 1 : 1 (v/v).

B-5.2.7 Hydrochloric Acid Solution — 1 : 1 (v/v).

B-5.3 Procedure

B-5.3.1 Weigh accurately 6 to 10 g of the finely powdered sample and transfer into the flask of the Krupp apparatus. The quantity of sample depends on the probable sulphur content of the type of ore being tested.

B-5.3.2 Add 2 g of boric acid and 2 g of pure quartz powder (iron free), wash the sides of the flask with little water and shake the flask to mix the contents.

B-5.3.3 Fill upper part of the apparatus with water so that the water remains upto the level of side opening of the glass tube. Add 10 ml of stannous chloride solution and immediately close the ground glass stoppered part of the apparatus. Fix the apparatus on to a retort stand and connect its outlet tube to the gas washing bottle that contains about 50 ml of hydrogen sulphide absorption solution and 100 ml of water.

B-5.3.4 Add about 60 ml of hydrochloric acid solution [1 : 1 (v/v)] into the flask through thistle funnel and slowly heat the contents of the flask applying slight suction through the other end of the gas washing bottle.

B-5.3.5 Ensure that the hydrogen sulphide gas evolved due to the reaction is transferred to the gas washing bottle by checking the suction periodically during the test. Boil the contents of the flask for 15 minutes.

NOTE — Water in the upper tube of the apparatus will also start boiling during the last stage of heating indicating complete transfer of hydrogen sulphide gas evolved to the absorption solution.

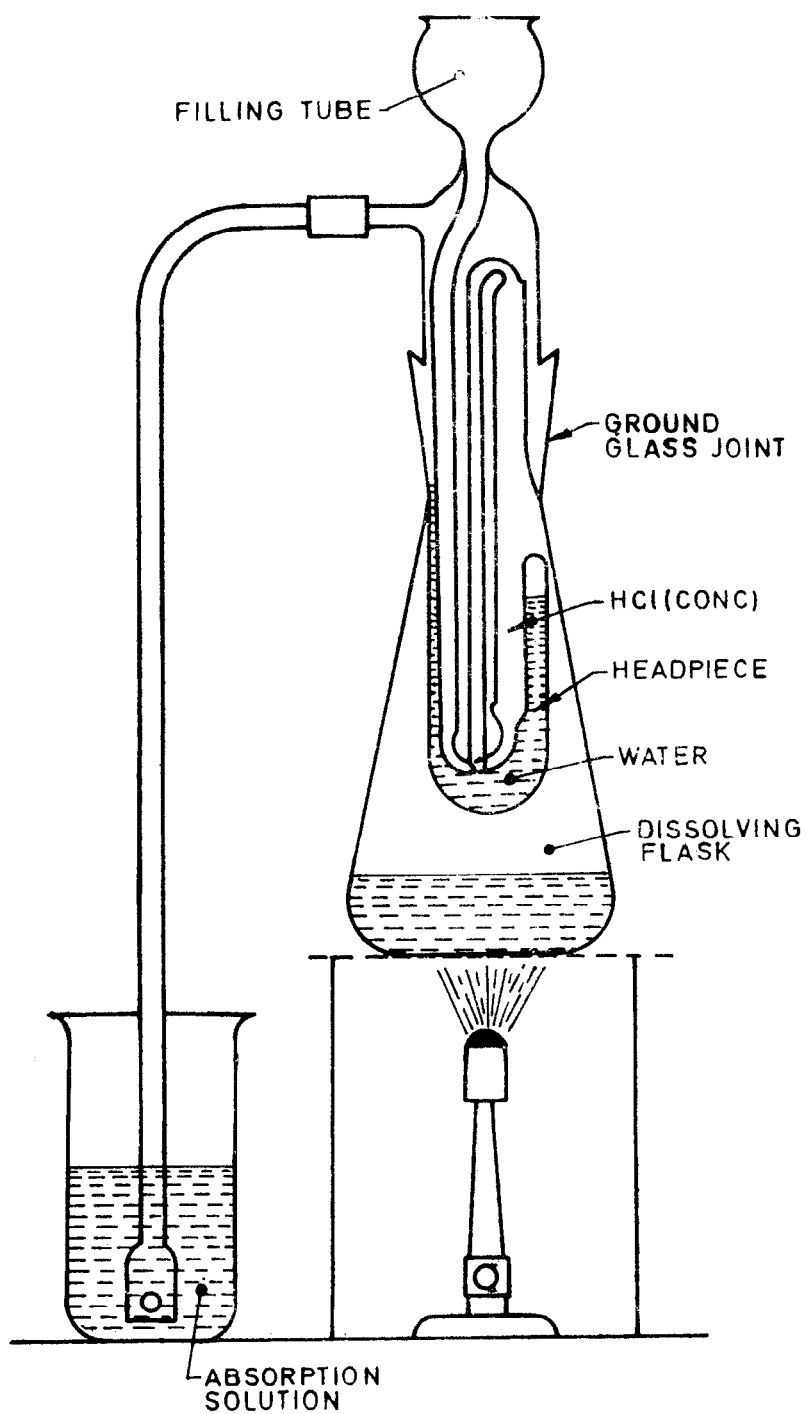


FIG. 1 APPARATUS FOR SULPHUR DETERMINATION

B-5.3.6 Break the vacuum after disconnecting the gas washing bottle from the apparatus. Transfer its contents into a 500-ml capacity conical flask, add 10 ml of potassium iodate solution, 40 ml of hydrochloric acid solution [1 : 3 (v/v)] and titrate with sodium thiosulphate solution, using starch as indicator.

B-5.4 Calculation

$$\text{Sulphur (as S), percent by mass} = \frac{(a - b)}{M} \times 0.1603$$

where

a = volume in ml of 0.1 N potassium iodate solution added,

b = volume in ml of 0.1 N sodium thiosulphate solution consumed in titration, and

M = mass in g of the material taken for the test.

B-6 DETERMINATION OF ORGANIC MATTER

B-6.1 Outline of the Method

The sample is treated with trichlorotrifluoro ethane and slightly heated when the organic matter is dissolved. The mixture is filtered and the dissolved organic matter is determined by evaporating the filtrate to dryness and weighing the residue.

B-6.2 Reagents

B-6.2.1 Trichlorotrifluoro Ethane

B-6.3 Procedure

B-6.3.1 Weigh accurately about 15 to 20 g of the finely powdered dry sample in a platinum dish, add 50 ml of trichlorotrifluoro ethane and heat the contents carefully on a water bath at about 50 °C to small volume.

B-6.3.2 Add further 50 ml of trichlorotrifluoro ethane and continue heating, till about 20 ml of trichlorotrifluoro ethane remains. Filter the contents through Whatman No. 42 or equivalent filter paper and collect the filtrate in a tared platinum dish. Evaporate the solution slowly on a water bath to complete dryness and finally in an oven at 80 °C. Cool the dish and re-weigh. Carry out a blank simultaneously.

B-6.4 Calculation

$$\text{Organic matter, percent by mass} = \frac{(M_1 - M_2)}{M} \times 100$$

where

M_1 = mass in g of residue after evaporation,

M_2 = mass in g of residue in blank determination, and

M = mass in g of the material taken for the test.

B-7 DETERMINATION OF SILICA (AS SiO_2)

B-7.0 Two methods are prescribed, namely, gravimetric method and photometric method. In case of dispute the photometric method shall be the referee method.

B-7.1 Gravimetric Method

B-7.1.1 The method is the same as prescribed in 8 of IS 2411 : 1963.

B-7.2 Photometric Method

B-7.2.0 Outline of the Method

The sample is fused with anhydrous sodium borate and the melt is dissolved in dilute hydrochloric acid. Silica is determined photometrically after extraction of the silicomolybdate complex with normal butyl alcohol. Photometric measurement of the extract is made at 400 nm.

B-7.2.1 Reagents

B-7.2.1.1 Ammonium molybdate solution — (100 g/l).

Dissolve 100 g of ammonium-heptamolybdate [$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$] in 500 ml of water, dilute to 1 000 ml and mix.

B-7.2.1.2 Silica

Heat pure silicic acid in platinum crucible to expel combined water by gradually increasing temperature to 1 050 °C. Maintain at 1 050 °C for at least 5 minutes. Cool to room temperature in a desiccator.

B-7.2.1.3 Sodium borate ($\text{Na}_2\text{B}_4\text{O}_7$) — Anhydrous powder, low-silica content.

NOTE — If low silica sodium borate is not available, prepare the reagent as follows:

Transfer 247 g of boric acid to a large platinum dish. Expel water by gradually increasing the temperature to about 1 000 °C. When effervescence ceases, gradually introduce 106 g of sodium carbonate into the molten mass. Maintain at a temperature of about 1 000 °C until a clear melt is obtained.

B-7.2.1.4 Sample Preparation

Grind the material to pass through 150 micron IS Sieve. Dry at 105 to 110 °C for a minimum of 1 h.

B-7.2.1.5 Procedure

Transfer 7 g of sodium borate ($\text{Na}_2\text{B}_4\text{O}_7$) to each of six 25-ml platinum crucibles. Form a cavity in the centre of the flux. Into crucibles 1 and 2 weigh 0.100 to 1 g of the dry sample. Choose sample quantities to provide from 5 to 10 mg of SiO_2 . Into crucibles 3 and 4 weigh

10.0 mg of silica reagent. Crucibles 5 and 6 serve as blanks. Mix the contents of the crucibles with a platinum or polyethylene rod. Transfer adhering particles to the crucible. Cover the crucible and heat gently until moisture is expelled. Increase the temperature until complete fusion results.

Transfer the platinum cover to 400-ml polyethylene beaker containing 150 ml water and 25 ml hydrochloric acid [1 : 1 (v/v)]. Cool the crucible, then pour the melt dropwise into the beaker so that most of the flux settles on the crucible cover (see Note 2). Transfer the cooled crucible to the beaker. Cover the beaker with a polyethylene sheet and secure it to the beaker with a rubber band.

Place the beaker on a steam bath and swirl occasionally until the melt is completely dissolved (see Note 3). Cool, remove and rinse the platinum crucible and cover. Add the washings to the beaker. Transfer the solution to a 250-ml volumetric flask. Rinse the beaker and add the rinsings to the flask. Dilute to the mark, mix and examine the solution for any insoluble material (see Note 4). Transfer the solution to a dry polythylene bottle.

Transfer 50 ml aliquots of the blank and sample solution to a 200-ml capacity polyethylene beaker.

Transfer 10.0, 20.0, 30.0, 40.0 and 50.0 ml aliquots of the standard solutions to 200-ml polyethylene beakers, dilute, if necessary, to a 50 ml volume with the remaining blank solution.

Determine the pH of the blank standard and sample solutions using a PH meter. If the pH of the solutions lies between 0.5 and 0.9 and within 0.1 unit of each other, proceed as under. In case the PH lies outside these parameters, adjust the pH with hydrochloric acid [1 : 1 (v/v)].

Add, while stirring 10 ml of ammonium molybdate solution. Allow 10 minutes for colour development, then dilute to 100 ml. Transfer the solution to 250-ml separatory funnel and add 25 ml of cold sulphuric acid [1 : 1 (v/v)]. Add 75 ml of normal butyl alcohol and shake vigorously for 1 minute. Allow the phases to separate and discard the acid (lower) layer. Add 20 ml of sulphuric acid [1 : 99 (v/v)] to the separatory funnel. Shake for 30s, allow the phases to separate and discard the acid layer. Repeat the washing twice more.

NOTES

1 A Meker burner or a muffle furnace maintained at 1 000 °C may be used for this purpose.

2 This prevents damage to the beaker.

3 Complete dissolution of the melt requires about 2 h. In cases of incomplete dissolution, a new sample must be taken.

B-7.2.1.6 Transfer the butyl alcohol phase to a dry 100-ml volumetric flask. Wash the separatory funnel twice with 1 or 2 ml portions of butyl alcohol and add the washings to the volumetric flask. Add 1 ml of ethyl alcohol, dilute to volume with buthyl alcohol, and mix.

B-7.2.1.7 Adjust the photometer to the initial setting using water as the reference solution. While maintaining this setting, take photometric readings of the blank standard and sample solutions using a light band centered at approximately 400 nm.

B-7.2.1.8 Preparation of calibration curve

Subtract the average absorbance of the blank solution from the average absorbance of each standard solution and plot the net absorbances against milligrams of silica per 100 ml of solution.

B-7.2.1.9 Calculation

Subtract the average absorbance of the blank solutions from absorbances of the sample solutions. Convert the net absorbance of the sample solutions to milligrams of silica by means of the calibration curve. Calculate the percentage of silica as follows:

$$\text{Silica (as SiO}_2 \text{), percent by mass} = \frac{A}{B} \times 10$$

where

A = mass in mg of silica found in the aliquots used, and

B = mass in g of sample represented by the aliquot.

B-8 DETERMINATION OF CHLORIDE

B-8.1 Outline of the Method

The sample is boiled with water to bring chlorides into solution and the solution is filtered through filter paper. Chloride in the filtrate is then determined volumetrically.

B-8.2 Reagents

B-8.2.1 Calcium Carbonate — solid.

B-8.2.2 Standard Silver Nitrate Solution — 0.02 N.

B-8.2.3 Potassium Chromate Indicator Solution — 1 percent (m/v) in water.

B-8.2.4 Dilute Nitric Acid — 50 percent (v/v), approximately.

B-8.2.5 Borax — power.

B-8.2.6 Standard Chloride Solution

Accurately weigh 2.101 g of potassium chloride, previously dried in an oven 135 °C for several

hours and cooled in a desiccator. Dissolve in water in one-mark volumetric flask of 1 000 ml capacity and make up the volume with water. One millilitre of solution contains 1 mg of chloride.

B-8.3 Procedure

B-8.3.1 Weigh accurately 10.0 g of the dried material (see B-2.1) in a 400-ml beaker and add about 1 g of calcium carbonate. Add about 150 ml of water and heat to boiling. Boil for about 10 minutes and filter. Wash the residue with hot water 2 or 3 times and collect washings in a 500-ml conical flask.

B-8.3.2 Add 2 ml of potassium chromate indicator solution and then nitric acid drop by drop until the indicator just begins to change colour from yellow to orange. Then add about 1 g of borax and mix thoroughly. The indicator will become yellow again. Titrate with thorough shaking against standard silver nitrate solution to the appearance of a brick red tinge in the yellow solution.

B-8.3.3 In another 500-ml conical flask take 2 ml of potassium chromate indicator solution and 1 ml of standard chloride solution. Dilute to about 180 to 190 ml with water and then proceed exactly as in B-8.3.2. The brick red tinge in this titrated solution should match as closely as possible the tinge produced in the earlier titration.

B-8.4 The material shall be deemed to have passed the test if the titre of silver nitrate in the case of test solution is equal to or less than the titre in the case of standard solution.

B-9 DETERMINATION OF BERYLLIUM

B-9.1 Outline of the Method

The ignited precipitate obtained in the determination of mixed oxides (by ammonia precipitation) is fused with potassium pyrosulphate and the cooled cake is dissolved in acidified water. The solution is then poured in sodium hydroxide solution, filtered, the insoluble residue is washed thoroughly with hot solution of sodium hydroxide and the filtrate is then cooled and made to known volume. Beryllium in the solution is estimated colorimetrically.

B-9.2 Reagents

B-9.2.1 Potassium Pyrosulphate — powder.

B-9.2.2 Standard Beryllium Solution

Dissolve 4.187 g of anhydrous beryllium sulphate in water acidified with a little sulphuric acid. Filter through filter paper (Whatman No. 40 or equivalent) into 100-ml volumetric flask, make up the volume and mix thoroughly. One millilitre of this solution is equivalent to

10 mg of beryllium (Be). Transfer 20 ml aliquot of this solution to 1 000-ml volumetric flask, add 1 ml of dilute sulphuric acid (1:1), dilute to the mark and mix thoroughly. One millilitre of this solution is equivalent to 0.2 mg of beryllium (Be). Take 25 ml aliquot of this solution and dilute it to 1 000 ml. One millilitre of this solution is equivalent to 0.005 mg of beryllium (Be).

B-9.2.3 Sodium Hydroxide Solution — 2 N.

B-9.2.4 Dilute Sulphuric Acid — 5 N.

B-9.2.5 Citrate — Borate Buffer Solution

- Add 288 g of boric acid and 512 g of citric acid to 2 000 ml of water and stir to dissolve most of the acids. Cool the solution.
- Dissolve 950 g of sodium hydroxide in 1 000 ml of water. Cool and add to the cooled solution (a) slowly with constant stirring. Cool, dilute to 4 000 ml and filter.

B-9.2.6 4 (p-Nitrophenyl-azo) Orcinol Solution — Dissolve 0.3 g of the material in 1 000 ml of 0.1 N sodium hydroxide solution by stirring with a mechanical stirring device for five hours; filter and store in a brown bottle.

B-9.3 Procedure

B-9.3.1 Fuse slowly at the lowest heat, the precipitate of combined oxides obtained in the determination of mixed oxides, with about 1 g of potassium pyrosulphate, cool and dissolve the cake in about 40 ml of water and 10 ml of sulphuric acid. Boil, if necessary, to ensure full dissolution. Pour the resultant solution with stirring in about 50 ml of hot sodium hydroxide solution and again boil for a minute. Filter through filter paper (Whatman No. 41 or equivalent) and wash the residue 2 or 3 times with hot sodium hydroxide solution. Combine the filtrate and washings, and evaporate to 30 to 50 ml.

B-9.3.2 Transfer the solution to a 100-ml volumetric flask and add dilute sulphuric acid until the pH is about 5 to 6. Add 10 ml of citrate borate buffer; mix and let stand for 5 minutes, add exactly 10 ml of 4 (p-nitrophenyl-azo) orcinol solution, dilute to the mark, mix well and let stand for 10 minutes for full development of colour.

B-9.3.3 In another 100-ml volumetric flask, take 10 ml of standard beryllium solution and proceed exactly as in B-9.3.2.

B-9.4 The material shall be deemed to have passed the test if the red brown colour in case of test solution is not greater than that in the case of standard solution.

ANNEX C

(Foreword)

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